

REMARKS

Status of Claims

Claims 9 and 12 are cancelled. Claims 7, 8, 10, 11 and 13-38 are withdrawn from consideration. Claims 1-6 and 39 are present for examination.

Prior Art Rejection

Claims 1-6 and 39 stand rejected under 35 U.S.C. § 103 as unpatentable over Seuntjens (6,397,454) in view of Sukeyuki (JP07-0169342). The Seuntjens reference is the primary reference cited by the Examiner, and the Sukeyuki reference is cited for disclosing a metal matrix containing silver for better heat and electrical conductivity.

The Examiner's rejections are respectfully traversed.

As understood from Seuntjens, staybribe solder is oxidized to provide SnO_2 to serve as a layer of high resistance. As such the reference fails to disclose a layer of high resistance formed of strontium vanadium oxide, as disclosed in the present invention.

The present invention and the reference provide different layers of high resistance and hence different critical current densities. Critical current density J_c is defined by the following expression:

$J_c = \text{critical current value}/\text{superconducting wire's area in cross section}$

By contrast the reference's Fig. 9 shows J_{o_e} defined by the following

$J_{o_e} = \text{critical current value with magnetic field being zero}/\text{wire's area in cross section}$

wherein the wire's area in cross section includes the, superconductor's area in cross section, the silver sheath's area in cross section, and the high-resistance element's area in cross section.

In the present invention's embodiment, /critical current density J_c is $22,000 \times 10^4 \text{ A/m}^2$. In the reference, J_{o_e} , as understood from Fig. 9, is maximally $2,130 \text{ A/cm}^2$. In the reference, as understood from Fig. 8, the wire has an area in cross section approximately

twice that of the superconducting filament. As such, J_c in the reference multiplied by two will be the critical current density J_c in the reference. ($J_c = J_{oe}$). Consequently in the reference critical current density $J_c = 2 \times 2,130 \times 104 \text{ A/m}^2 = 4,260 \times 10^4 \text{ A/m}^2$. Thus the present embodiments J_c is approximately five times that of the reference. This is presumably because in the reference the layer of high resistance (SnO_2) adversely affects the superconductor. In the present invention a high resistance element that does not adversely affect superconductor can be used to exhibit a high critical current value. Seuntjens fails to disclose that to obtain a high critical current value a layer of high resistance formed of strontium vanadium oxide is used. Please note that as indicated in the enclosed document published by American Super semiconductor Corporation, who is an assignee of the Seuntjens patent, critical current density has a typical value of $15,000 \times 10^4 \text{ A/m}^2$ and best value of $55,000 \times 10^4 \text{ A/m}^2$.

In view of the comments set forth above, it is submitted that applicant's claims readily distinguish applicant's invention from the applied prior art and are patentable thereover.

In view of the arguments set forth above, it is submitted that applicant's claims are patentable over the prior art.

The application is believed to be in condition for allowance and an early indication of same is earnestly solicited.

The Commissioner is hereby authorized to charge any additional fees which may be required regarding this application under 37 C.F.R. §§ 1.16-1.17, or credit any overpayment, to Deposit Account No. 19-0741. Should no proper payment be enclosed herewith, as by a check being in the wrong amount, unsigned, post-dated, otherwise improper or informal or even entirely missing, the Commissioner is authorized to charge the unpaid amount to Deposit Account No. 19-0741. If any extensions of time are needed for timely acceptance of papers submitted herewith, Applicant hereby petitions for such extension under 37 C.F.R. §1.136 and authorizes payment of any such extensions fees to Deposit Account No. 19-0741.

Respectfully submitted,

Date January 12, 2004

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Progress in Superconducting Performance of Rolled Multifilamentary Bi-2223 HTS Composite Conductors

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Abstract—Significant enhancements in critical current densities in rolled multifilamentary Bi-2223 HTS composite conductors have been achieved using the powder-in-tube (PIT) technique. At 77 K and self field, oxide critical current densities (J_c) of 55 kA/cm², overall or engineering critical current densities (J_e) of 15 kA/cm², and critical currents (I_c) of 125 A have been achieved in different rolled multifilamentary composites. Progress in achieving such high electrical performance is believed to stem in part from an improvement of grain connectivity by reducing weak links. The J_c dependence on magnetic field (B) and the degree of c-axis texture of these high quality conductors have been investigated at various temperatures. Our results also demonstrate that the critical current retention in magnetic field can be independently controlled from the self field critical current density, suggesting that flux pinning improvements and weak link reductions can be separately engineered into Bi-2223 composites fabricated using manufacturable processes.

I. INTRODUCTION

A tremendous amount of effort has been made to improve the critical current densities of commercially interesting Ag sheathed Bi-2223 HTS multifilamentary conductors using the powder-in-tube process. For rolled multifilamentary composites, J_c values in the range of 40 to 44 kA/cm² at 77 K and self field have been reported [1] - [2]. In contrast, J_c values of 50 to 69 kA/cm² have been reported for pressed monofilamentary samples, [1], [3] - [5]. Although the J_c performance of the pressed monofilaments is higher than that of the rolled multifilaments in these previous works, there are compelling reasons to further pursue the latter option. Rolling is a scaleable and practical process for making long and continuous lengths of HTS conductor. Moreover, the strain tolerance of multifilamentary composites is superior to that of monofilamentary composites. As a final consideration for the practical use of

HTS wire, high J_e and I_c performance is required across long lengths in a magnetic field.

To enhance the self field J_c of the Bi-2223 composites, the connectivity between grains must be improved by reducing the number of weak links. A high degree of c-axis texture and clean grain boundaries are the most effective means of mitigating weak links [5] - [8].

Due to the relatively poor flux pinning of current generation Bi-2223 composites, their J_c decreases markedly in high magnetic fields as temperature increases. Therefore, application of Bi-2223 conductors in high magnetic fields is currently limited to low temperatures. To enhance the self field J_c of Bi-2223 composites, improvements in the capacity to pin magnetic flux, either by enhancing electronic coupling between Cu-O layers or introducing appropriate defect structures, must be made. The introduction of splayed columnar defects, dislocations, and secondary phase precipitates are thought to enhance flux pinning [9] - [11]. In addition, coupling may be modified via intrinsic doping effects [12]. Recently, Parrell et al. [8], [13] reported that slow cooling during the final heat treatment improves both flux-pinning and connectivity of Bi-2223 composites.

In this article, we report new levels of J_c , J_e , and I_c performance for laboratory scale, rolled multifilamentary conductors (< 1 meter lengths). In addition, the $J_c(B,T)$ dependencies have been characterized in magnetic fields up to 10 T at temperatures between 4.2 and 77 K. Finally, we provide an interpretation of the enhanced self field and in-field performance in the context of connectivity and ‘effective’ flux pinning.

II. EXPERIMENTAL

Multifilamentary composites were fabricated using the powder-in-tube technique. The stoichiometry of our powder is $\text{Bi}_{1.8}\text{Pb}_{0.3}\text{Sr}_{1.9}\text{Ca}_{2.0}\text{Cu}_{3.1}$. Sequential thermomechanical processing in which each iteration consists of a rolling plus a heat treatment sequence was used to promote 2223 phase formation, texture, and densification.

Manuscript received August 25, 1996.

Transport critical current ($1 \mu\text{V}/\text{cm}$) measurements in different magnetic fields and at various temperatures were performed using a standard four probe technique. Transport J_c and J_e were determined by dividing the I_c by the total cross-sectional area of the oxide core and conductor, respectively. The dependence of J_c on the angular orientation of the applied magnetic field was determined using techniques described in [14].

III. RESULTS

1. Progress in J_c , J_e , and I_c

In the past year the superconducting performance of our rolled multifilamentary composite conductors has significantly increased. The results of Fig. 1 represent the improvement of laboratory scale Bi-2223 conductors made by a scalable rolling process at American Superconductor Corporation. On average the J_c results measured at 77 K in self field, has improved about $11 \text{ kA}/\text{cm}^2$ per year over a five year period. Given the complexity of the Bi-2223 PIT process, it is remarkable that the time rate of performance increase for multifilamentary composites made using scalable techniques is approximately linear over an extended period of time. Moreover, it is highly encouraging to HTS wire developers that there is no apparent decrease in the recent rate of improvement indicated in Fig. 1.

The best J_c performance has now reached the $55 \text{ kA}/\text{cm}^2$ level (77 K and self field) for rolled 85 filament composites. More importantly, the J_c standard deviation σ of 12 samples is less than 2 %. These results represent the first time that the electrical performance of commercially interesting multifilamentary wires has established parity with that of pressed monofilamentary samples [1], [3] - [5]. We have also achieved J_e values (77 K and self field) of $15 \text{ kA}/\text{cm}^2$ ($\sigma = 0.5 \%$ for 8 samples) in rolled 85 filamentary composite conductors. High current capacity samples with I_c values of 125 A ($\sigma = 1.7 \text{ A}$) have been measured at 77 K and self-field for 313 filament composite conductors. These high

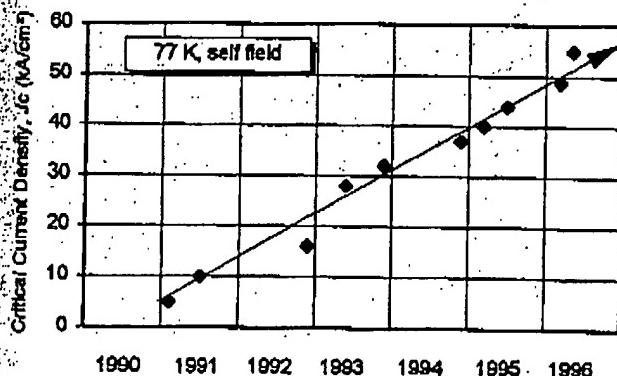


Fig. 1. Plot of J_c performance vs. time for rolled multifilamentary Bi-2223 conductors at American Superconductor Corporation.

I_c conductors have J_c values of $39.7 \text{ kA}/\text{cm}^2$. All of these results are obtained at self field. The true zero field J_c , J_e , and I_c values are likely to be at least 10 % higher than the self field results [6], [15].

Fig. 2 summarizes the $J_c(B, T)$ dependencies of one of the high J_c samples in the $B \parallel$ tape plane (Fig. 2a) and $B \perp$ tape plane (Fig. 2b) orientations. At 75 K, J_c values of $45 \text{ kA}/\text{cm}^2$ in 0.1 T , $32 \text{ kA}/\text{cm}^2$ in 0.3 T , and $15 \text{ kA}/\text{cm}^2$ in 1 T are retained in the $B \parallel$ tape plane direction. Although the self field J_c value of this 85 filament conductor is lower than that previously reported for pressed monofilamentary samples ($66 \text{ kA}/\text{cm}^2$ at 77 K) [5], its J_c at 1 T is similar to that of the pressed samples ($14.5 \text{ kA}/\text{cm}^2$ at 77 K and 1 T). Our earlier study [1] suggests that this may be due to a smaller fraction of weak links in the rolled samples as compared to the pressed samples. At 64 K and $B \parallel$ tape plane, the self field J_c of the sample is $86.5 \text{ kA}/\text{cm}^2$, and $42.3 \text{ kA}/\text{cm}^2$ is retained at 1 T . Even in the $B \perp$ tape plane direction, the sample has J_c of $18 \text{ kA}/\text{cm}^2$ and $42 \text{ kA}/\text{cm}^2$ at 0.1 T and 75 K and 64 K, respectively. In addition, the J_c is $295 \text{ kA}/\text{cm}^2$ at 4.2 K .

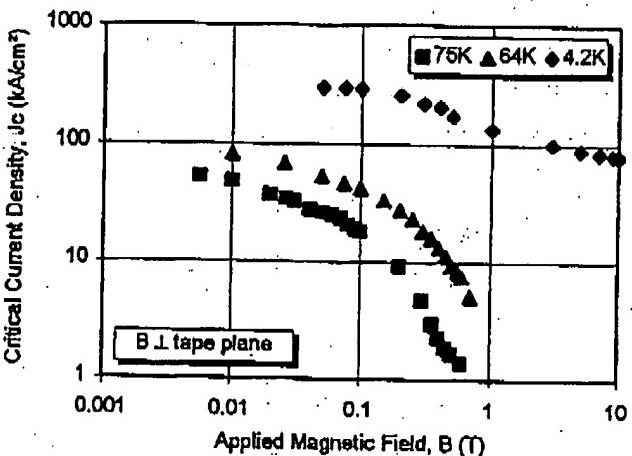
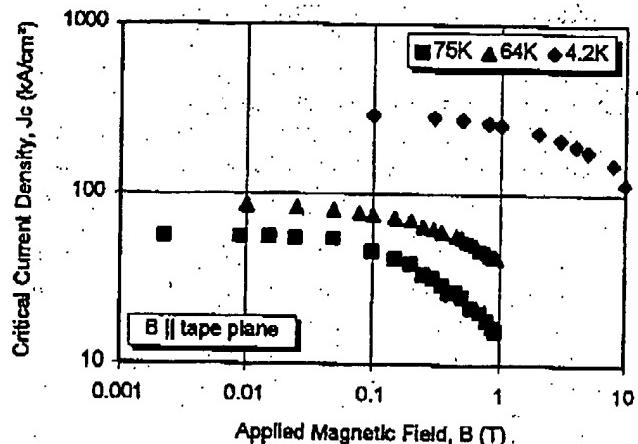


Fig. 2. The magnetic field dependence of J_c (a) for $B \parallel$ tape plane and (b) for $B \perp$ tape plane at temperature range from 4.2 to 75 K for the rolled 85 filament conductors.

self field. At 4.2 K and 10 T, the J_c is almost 80 kA/cm^2 for $B \perp$ tape plane. These results are very promising for many commercial applications. For example, transmission cables at 64 - 77 K and low field ($< 0.1 \text{ T}$), transformers at 50 - 77 K and moderate field (0.1 - 0.3 T), and large motors at 20 - 30 K and high field ($> 1\text{ T}$).

B. Connectivity and Effective Flux Pinning Improvements

To reduce weak links, the c-axis texture of the Bi-2223 polycrystals must be improved. The degree of c-axis texture of these Bi-2223 polycrystals can be described by their mean misorientation angle. An estimate for this misorientation angle (Φ) can be made using two different techniques. In the first method, the values of $B \parallel$ tape plane and $B \perp$ tape plane at 75 K (obtained in Fig. 2a and 2b) are rescaled by $\sin(\Phi)$ and $\cos(\Phi)$, respectively, to characterize the average c-axis component along the non-perfectly textured grains. The Φ value is chosen to collapse the I_c curves for the $B \parallel$ and $B \perp$ orientations onto each other, as seen in Fig. 3. In this manner, we obtain a misorientation angle of about 7° for the 85 filament sample with self-field J_c of 55 kA/cm^2 . In the second method, the I_c of the same sample is measured as a function of the angle θ between the magnetic field and the tape plane by physically rotating the sample in a constant amplitude magnetic field of 0.3 T and 75 K [14]. The I_c data are plotted against the component of $B \perp$ tape plane ($0.3T\sin\theta$). Thus, the misorientation angle is determined as the angle at which the $I_c - 0.3T\sin\theta$ curve deviates significantly from the previous two data sets, as shown in Fig. 3. This procedure yields a misorientation angle of about 8° , in good agreement with that obtained with the first method. For pressed monofilamentary samples with J_c in the range of 10 - 20 kA/cm^2 (77 K, self field), several groups [7], [13], [16] have reported typical Φ values in the

range of 9 - 12° determined by both x-ray rocking curve and J_c - magnetic field angular dependence techniques. There is no obvious relationship between J_c and Φ values for these pressed monofilament samples. However, Kobayashi et al. [17] clearly showed that the J_c values for multifilamentary tapes increase from 15 to 33 kA/cm^2 as Φ decreases from 11° to 8° . The Φ value of their sample with a J_c of 33 kA/cm^2 (8°) is similar to our sample with a J_c of 55 kA/cm^2 . This indicates that the degree of texture is not the only reason for obtaining a smaller fraction of weak links.

Fig. 4 shows the magnetic field dependence of I_c for two rolled multifilamentary samples whose self field J_c differs by a factor of two (22.5 to 45 kA/cm^2). These two samples have the same oxide core cross-section area and total conductor cross-section area, and thus, the relationship between their I_c corresponds directly to that for the J_c . Using a technique similar to the one described above for determining Φ , the $B \parallel$ tape plane data have been scaled by the appropriate factor $\sin(\Phi)$, where $\Phi = 8.5^\circ$, which collapses that data set onto the I_c data for $B \perp$ tape plane. The scaling factor also characterizes the mean misorientation of the Bi-2223 platelets to the rolling direction [7], [14]. The Φ values are found to be about 8.5° for both samples. This is clear evidence that the degree of c-axis texture is not the only factor that affects weak links reduction, and hence, J_c performance. For the high J_c sample, it appears that modifications to the processing have substantially reduced the number of weak links, either by cleaning the grain boundaries or by otherwise better connecting the grains. In either case, the useful cross-section carrying currents has increased.

We have also improved the current carrying capability in magnetic field in our composites. At 64 K, the I_c magnetic field retention of three rolled 85 filament tapes with 77 K self field J_c values varying from 22.5 to 45 kA/cm^2 is shown in Fig. 5. These samples have the same oxide core cross-

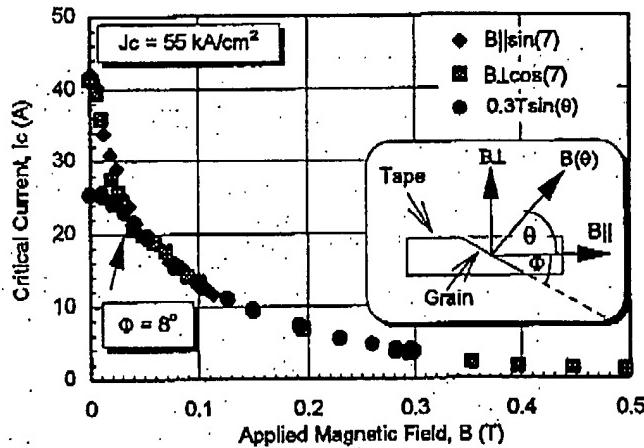


Fig. 3. I_c as a function of magnetic field angle in 0.3 T plotted against $B\sin\theta$ and of the two principal magnetic field orientations rescaled for 7° angle for the rolled 85 filament sample at 75 K, showing degree of texture via misorientation angle estimations.

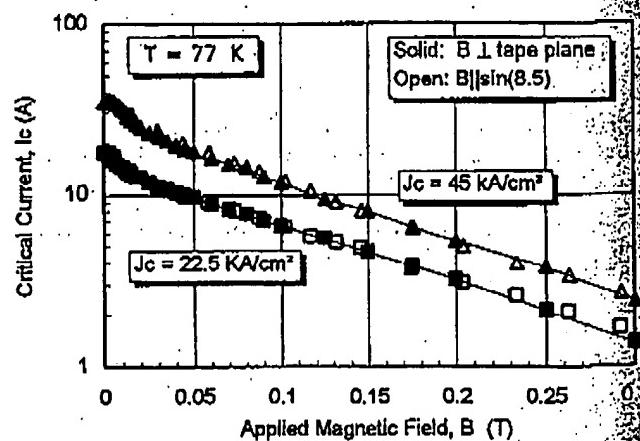


Fig. 4. The dependence of I_c on magnetic field for two 85 filaments at 77 K, showing weak link reduction. The $B \parallel$ field magnitude has been scaled by $\sin(8.5)$ to account for the fitted misorientation of the grains.

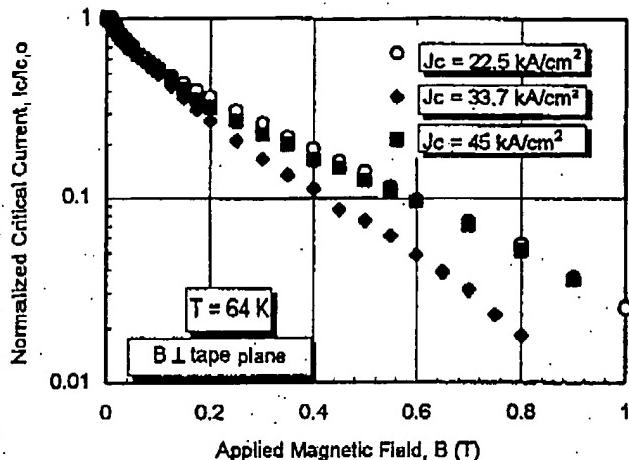


Fig. 5. The retention of critical current relative to the self field value at 64 K for three rolled 85 filamentary conductors with J_c values of 22.5, 33.7, and 45 kA/cm^2 , showing independence of connectivity and flux pinning.

section area and total conductor cross-section area, and thus, the relationship between their I_c corresponds directly to that for the J_c . As seen in Fig. 5, the low J_c sample has $J_c(B)$ retention comparable to that of the high J_c sample. However, the median J_c sample has poor $J_c(B)$ retention. These three sets of data unambiguously show that the self field J_c can be decoupled from the relative level of retention in magnetic field. By understanding the mechanisms underlying these effects it should therefore be possible to independently engineer flux pinning improvements and weak link reductions in Bi-2223 conductors.

IV. SUMMARY

The superconducting performance of rolled multifilamentary Bi-2223 HTS composite have been significantly improved using a manufacturable powder-in-tube technique. At 77 K and self field, oxide critical current densities of 55 kA/cm^2 , engineering critical current densities of 15 kA/cm^2 , and critical currents of 125 A have been achieved in different rolled multifilamentary composites. These results represent the first time that the J_c of commercially interesting multifilamentary wires has established parity with that of the best pressed monofilamentary samples.

American Superconductor Corporation has also made rapid progress in translating these performance improvements into long length wires. At 77 K and self field, engineering critical current densities, J_e of greater than 8 kA/cm^2 have already been achieved in consecutive long length production wires of over several hundred meters.

The enhancement of these self field values of the critical current density is believed to be due mostly to reducing weak links between Bi-2223 grains. In addition, we have improved the critical current retention in magnetic field by enhancing the 'effective' flux pinning of Bi-2223. Most

importantly, we have shown that flux pinning and weak link phenomena can be decoupled, so that improvements in flux pinning and reductions in weak links in Bi-2223 comp sites can be separately engineered to a much greater extent than was previously believed.

Both high temperature, low magnetic field and low temperature, high magnetic field performance levels are reaching those required to impact cable, transformer, and motor applications.

ACKNOWLEDGMENT

The authors are greatly indebted to the R&D and Manufacturing Teams at American Superconductor Corporation and to discussions in the Wire Development Group including individuals affiliated with UW, LANL, ORNL, ANL, NIST, and ASC. Special thanks are also given to Dr. A. P. Malozemoff for his stimulating discussions.

REFERENCES

- [1] Q. Li, S. Fleisher, P. J. Walsh, M. W. Rupich, W. L. Carter, E. R. Podlubny, and G. N. Riley, Jr., ICMC Conference, Columbus, OH, USA, July 17-21, 1995, in press.
- [2] K. Sato, K. Ohkura, K. Hayashi, T. Hikata, T. Kaneko, T. Kato, M. Ueyama, J. Fujikami, K. Muranaka, S. Kobayashi, and N. Saga, Proc. Inter. Workshop on Supercond., 1995, pp. 234.
- [3] Q. Li, K. Brodersen, H. A. Hjuler, and T. Fretoft, Physica C, 217(1993) pp. 360.
- [4] Y. Yamada, M. Satou, S. Murase, T. Kitamura, and Y. Kamimura, Proc. 5th Int. Symp. on Supercond. (ISS92), (1993) pp. 717.
- [5] M. Ueyama, T. Hikata, T. Kato, and K. Sato, Jpn. J. Appl. Phys., 30(1991) pp. L1384.
- [6] S. Fleisher, Q. Li, R. D. Parrella, P. J. Walsh, W. J. Michels, G. N. Riley, Jr., W. L. Carter, and B. Kunz, 8th IWCC, Kitakyushu, Japan, May 27-29, 1996, in press.
- [7] B. Hensel, J.-C. Grivel, A. Pollini, and R. Flükiger, Physica C, 205(1993) pp. 329.
- [8] J. A. Parrell, D. C. Larbalestier, G. N. Riley, Jr., Q. Li, R. D. Parrella, and M. Teplitsky, submitted to Appl. Phys. Lett., July 30, 1996.
- [9] H. Safar, J. H. Cho, S. Fleisher, M. P. Maley, J. O. Willis, J. Y. Coulter, J. L. Ullmann, P. W. Lisowski, G. N. Riley, Jr., M. W. Rupich, J. R. Thompson, and L. Krusin-Elbaum, Appl. Phys. Lett., 67(1995) pp. 130.
- [10] F. Marti, M. Däumling, and R. Flükiger, IEEE Trans. Appl. Supercond., 5(1995) pp. 1884.
- [11] K. Fossheim, E. D. Tuset, T. W. Ebbesen, M. J. Treacy, and J. Schwartz, Physica C, 248 (1995) pp. 195.
- [12] N. Adamopoulos, B. Soylu, Y. Yan, and J. E. Evetts, Physica C, 242(1995) pp. 68.
- [13] J. A. Parrell, D. C. Larbalestier, and S. E. Dorris, IEEE Trans. Appl. Supercond., 5 (1995) pp. 1275.
- [14] J. O. Willis, J. Y. Coulter, E. J. Peterson, G. F. Chen, L. L. Daemen, L. N. Bulaevskii, M. P. Maley, G. N. Riley, W. L. Carter, S. E. Dorris, M. T. Lanagan, and B. C. Prorok, Advances in Cryogenic Engineering, 40 (ICMC 1993) pp. 9.
- [15] L. Gherardi, P. Caraccino, G. Coletta, and S. Spreafico, submitted to Mater. Sci. and Engin. B., 1996.
- [16] Q. Y. Hu, H. W. Weber, H. K. Liu, S. X. Dou, and H. W. Neumuller, Physica C, 252(1995) pp. 211.
- [17] S. Kobayashi, T. Kaneko, T. Kato, J. Fujikami, and K. Sato, Physica C, 258(1996) pp. 336.